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ADSORPTION OF VAPOURS BY SILICA GEL
BY A DYNAMIC METHOD.

DISSERTATION

Submitted to the Board of University Studies of
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Philosophy.

by

Lawrence Hall Opdycke.
Baltimore, Md.
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ADSORPTION OF VAPOURS BY SILICA GEL BY A DYNAMIC METHOD.

I. Introduction.

The gel of Silicic Acid, its preparation, physical properties and its power of adsorbing vapours and dissolved substances have been described at length in the literature, and its recent adaptation to industrial processes has been developed, so that it is now a familiar substance and its properties quite generally understood. For references thereto vide: Graham, Trans. Phil. 151; Ann. 121 : Van Bemmelen, Zeit. f. anorg. Chem. 13 (1897); 18 (1898): Zsigmondy, Zeit. f. anorg. Chem. 71 (1911); Anderson, Zeit. f. Phys. Chem. 88, 1914; W. A. Patrick and others J. A. C. S. 42 (1920), 43 (1921).

All of the published work dealing with the adsorption of vapours by silica gel has been based on measurements made by the static method, i.e. the gel has been placed in contact with the vapour until equilibrium was reached and thereafter measuring the amount of vapour adsorbed and the resulting partial pressure. Such a method permits of most accurate measurements, but unless extraordinary precautions are exercised to exclude per-

manent gases the time that is necessary to reach equilibrium is exceedingly long. This has been shown in the case of sulphur dioxide adsorption by MacGavack and Patrick[1]. We were therefore surprised to discover that the results of the above careful static measurements made with the rigorous exclusion of all air were very accurately duplicated by passing mixtures of sulphur dioxide and air over the gel until saturation was reached. In other words, the dynamic method gave the same results as the static method that was carried out with the exclusion of all air.

Inasmuch as the dynamic method is much simpler from an experimental standpoint it was planned to measure the adsorption of a few vapours by this method. Anderson working in Zsigmondy's laboratory measured the adsorption of water, alcohol, and benzene by a static method, and although he worked in a vacuum it is obvious that he did not exercise sufficient precautions to remove the traces of air that interfere with the attainment of true equilibrium. We decided to apply the dynamic or air bubbling method with

1. McGavack and Patrick, J. A. C. S. 42 (1920)

a view of eliminating the so called hysteresis of the other observers.

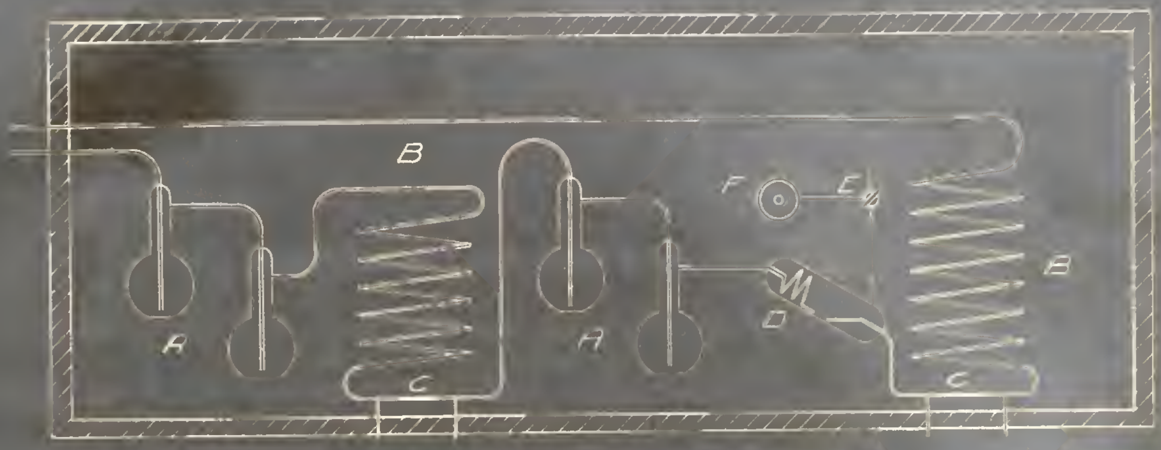
II. Apparatus.

The apparatus used was a slight modification of that devised for the purpose by W. A. Patrick and F. K. Bell in this laboratory. The essential plan is given in outline in Fig. I. The arrangement allowed air, saturated with the vapour under examination, to be mixed with the dry air free from the vapour. The resulting mixture had a vapour partial pressure dependent on the relative speeds of delivery of the two streams. This resultant mixture could be varied at will by devices to be explained and could be tapped off for ultimate analysis of vapour content and from that the partial pressure determined by vapour density data.

Figure I shows a general arrangement of apparatus in water thermostat. An automatic electric regulator and cooling coils maintained the temperature at 30° C. within 0.01 degree. The thermometer used was graduated in hundredth of a degree.

A,A represent gas bubbling devices which gave regula

FIG. 1



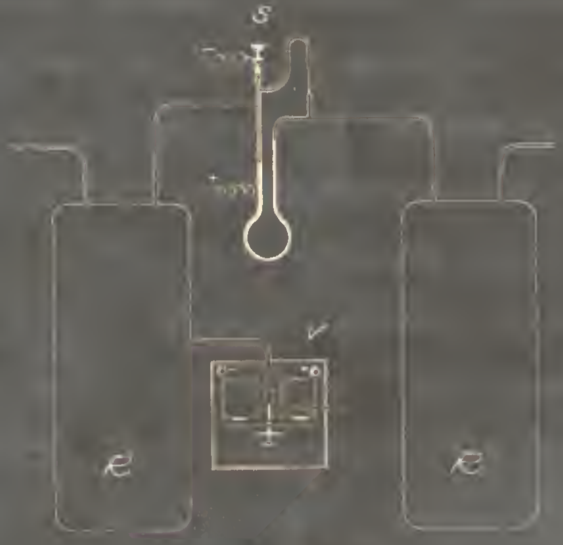


FIG. 3

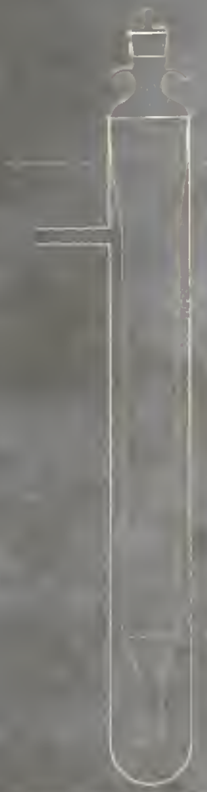


FIG. 2

flow. With a maximum delivery rate of 700 cc. per minute the saturation obtained was constant and by trial was found to be over 98 % with all three of the vapours used. B,B are coils through which the gas mixtures are passed to make certain of their temperature. C,C are flowmeters; in the manometers of which nitro benzol was used on account of its low vapour pressure and low density. D is a mixing bulb, F is a fitting for the adsorption bulb, provided with ground glass joints shown in detail in Fig. 2. E is a side tube connection extending vertically from the apparatus and through which samples of the gas were aspirated, measured and analyzed for vapour content.

Both streams of air were derived from a common reservoir. Before division the initial stream was cleaned and dried by passing it in series through four gas washing bottles containing concentrated H_2SO_4 . This was amply efficient since a P_2O_5 tower at the end of this series showed in one case no trace of gelatinous metaphosphoric acid after more than a month of almost continuous streaming during atmospheric conditions of high humidity. The first

and second washing bottles were freshly charged from time to time.

The flowmeter manometers C, C attached to the bath registered the streaming velocities by differences in pressure (measured by nitro benzol levels) between the source pressure on one side of a capillary tube in the course, and the atmospheric pressure on the further side. To sensitize this arrangement to dependance only on fluctuations in the atmospheric pressure large air reservoirs were interposed between the original current source and its inlet to the system. These reservoirs were separated by automatic devices whereby excessive source pressure was relieved by an outlet valve which was automatically closed when this was accomplished. At optimum conditions this opening and closing approximated a vibration. The device itself is a conversion of an ordinary thermoregulator relay and is shown in Fig. III.

Having once fixed a certain difference in manometer levels as determined for a "run", this could be established by adjustment of the contacts in regulator-flowmeter between the ultimate air reservoirs. If during a run the atmospheric

pressure changed, the contact points needed but a slight adjustment to compensate. Sparking at the contacts was reduced by a static condenser in parallel and the fouling of the Mercury surfaces was reduced by a superficial layer of high grade machine oil.

Stopcocks were introduced in three places in the outer parts to secure further control.

All connections were of rubber and glass and those under water were covered with a wax of elasticity and impermeability to water or the vapours used. The runs using Carbon Tetrachloride required a change of connections every three days owing to the swelling of the rubber but no leaks were observed at any time.

The experiments were all made at 30° C. If the room temperature fell far below this the mixtures of high saturation would cause condensation on that part of the adsorption bulb protruding above the water level of the thermostat. To overcome this a stream of dry air at about 40° C. was directed on that part.

The mechanism of the streaming and mixing control was not used to measure the vapour partial pressure, but simply as control . Samples of the vapour and air mixture,

after an initial preliminary running, were drawn by water aspirator through the side tube E , measured for one liter by a measuring flask and corrected for volume at room temperature to 30° C. These samples were all run through analysing tubes and vapour content by weight determined. Detail given under Procedure.

III. Materials.

1. The gel used for all the experiments was from one sample that of ( ) used by Patrick and McGavack , loc. cit. p. 959. It was analysed for water content and found to have 3.57% H_2O, having remained practically constant in a stoppered bottle for two years; its analysis then having given 3.51% H_2O . A gel of this water content has negligible water vapour tension at ordinary temperatures, the water being held other than mechanically, and for this reason would not lose weight by contact with air of no water content. Samples of from 3 to 5 gms. of uniform particle size were chosen.

2. The water used was distilled water.

3. The Ethyl Alcohol was from a highest grade and from a special sample obtained through the courtesy of the Industrial Alcohol Co. of Baltimore, Md. It was free from all impurities save H_2O, its content of which was known to be less than 0.05 % .

4. Carbon Tetrachloride used was fractionated six times from a C. P. grade and gave a constant boiling point of 77° C.

5. The Benzol was a high grade C. P. sample redistilled.

IV. Procedure.

A sample of gel was weighed in the adsorption bulb which was then unstoppered and placed in its container in the bath. The vapour currents both dry and saturated had already been regulated to relative speeds for a desired mixture. At constant temperature and pressure the gel in the bulb reached a constant weight in adsorbed vapour within a few hours. That equilibrium was reached was testified to by the smaller and smaller increments of weight.

At a mean value the weight varied ± 1 miligram due to unavoidable uncorrected fluctuations in the atmospheric pressure.

Between weighings the nitro-benzol levels were carefully maintained constant and samples of the vapour withdrawn at such rates that the end of the withdrawal coincided with the time set for adsorption-bulb weighings.

After each equilibrium point was reached the mixture was made richer in vapour until finally the stream of dry gas was entirely omitted. The gel sample remained the same of course throughout the experiments with any one vapour. From the saturation point the sample was subjected to successive decrements of the vapour partial pressure in order to test reversibility.

Analysis of the Vapour Mixtures.

1. For water two g.s. U tubes containing P_2O_5 were used.

2. For Ethyl Alcohol two Geissler Potash bulb

sets containing conc. H_2SO_4. The second tube in the series remained constant in weight throughout forty determinations.

3. For Benzol and Carbon Tetrachloride two U tubes as in (1) containing fresh dried Silica Gel were used. In these operations it was necessary afterward to pass dry air through these analysing tubes, or else subsequent passage of vapour with relatively large amounts of air would simply bring the analyser gel to equilibrium values instead of giving total content of the amount aspirated. By attention to this after each run it was possible to make ten to twenty determinations with but slight increase in the weight of the second tube.

Excepting the case of Water (see below) all the experiments showed that a true equilibrium was obtained. At these points the weight of the gel fluctuated interminably ± 1 miligram around a mean value. In all experiments the time was extended one hour beyond with intermediate weighings to test. In five instances this testing was continued for four hours with the same result.

With Water, equilibrium was very slowly reached

The reversed process showed some hysteresis from which the system apparently recovered on later dilution of the vapour. When the hysteresis was overcome in that manner equilibrium was not reached until after forty hours of five eight hour continuous runs. The water experiments were not repeated and the slight initial irreversibility observed might have been due to apparent equilibrium (although the above criteria were applied) from the great inertia of the system opposing desorption or the three points may represent metastable stationary points.

In the Alcohol and Carbon Tetrachloride experiments and at lower Water partial pressures the coincicence of adsorption and desorption curves is unmistakable showing equilibrium at all points indicated.

V. Tabulation of Experimental Results.

The following tables give the partial pressures used and the corresponding adsorbed quantities with other data to be used in the next section. Column 2 gives the amount by weight of vapour in one liter of gases at 760 mm and 30° C. The figures are averages of values that were checked to 1 % at the equilibrium point. Column 3 gives the partial pressures computed from Column 2 by vapour density data from Regnault and Young. Column 4 gives the value of P/P_0 or the corresponding pressures, P_0 being the saturation value at 30° C. Column 5 gives $\overset{\sigma}{P}/P_0$, σ being surface tension of the liquid used against its vapour. Column 6 gives $\frac{x}{m}$ values or weight of adsorbed material per gram of gel. Column 7 gives $\frac{v}{m}$ or volume (calculated from the liquid density) adsorbed per gram of gel.

TABLE I.

WATER VAPOUR.

Gel sample 4.1701 gm.

P_0 = 31.510 mm Hg. @ 30° C. $\sigma = 70 \frac{\text{dyne}}{\text{cm}}$ @ 30° C.

Exp.	Wt. Vapour	P mm	P/P_0	$P/P_0{}^{\sigma}$	$\frac{x}{m}$	$\frac{v}{m}$
1	0.0027	2.91	.092	6.46	0.064	0.064
2	0.0042	4.42	.140	9.82	0.082	0.082
3	0.0129	13.60	.431	30.21	0.2180	0.2182
4	0.0142	14.88	.472	33.06	0.2336	0.234
5	0.0177	18.55	.588	41.21	0.2674	0.2685
6.	0.0199	20.85	.662	46.32	0.2783	0.279
7	0.0296	31.00	.983	68.87	0.3133	0.315
8	0.0146	15.35	.487	34.10	0.2665	0.267
9	0.0130	13.68	.434	30.39	0.2533	0.254
10	0.0116	11.66	.370	25.91	0.2349	0.236
11	0.0077	8.13	.258	18.06	0.1452	0.145
12	0.0062	6.48	.205	14.40	0.1161	0.116
13	0.0034	3.55	.113	7.88	0.0751	0.075

TABLE II.

ETHYL ALCOHOL VAPOUR.

Gel sample 4.0268 gms.

P_0 = 78.4 mm @ 30° C. σ = 21.8 $\frac{\text{dyne}}{\text{cm}}$ @ 30° C.

Exp.	Wt. Vapour	P mm		P/P_0	$\overset{\sigma}{P/P_0}$	$\frac{x}{m}$	$\frac{v}{m}$	
1	0.0167	5.57	$\bar{2}.845$	.07	1.55	0.1197	0.1533	$\bar{1}.1$[illegible]
2	0.0255	8.75		.11	2.43	0.1325	0.1696	[illegible]
3	0.0380	13.04	$\bar{1}.204$	.16	3.62	0.1477	0.1891	$\bar{1}.276$
4	0.0530	18.18		.23	5.05	0.1625	0.2080	
5	0.0613	20.97	$\bar{1}.431$	.27	5.83	0.1718	0.2199	$\bar{1}.342$
6	0.0702	24.02		.308	6.73	0.1814	0.2322	[illegible]
7	0.0807	27.66	$\bar{1}.546$	.352	7.69	0.1909	0.2444	$\bar{1}.387$
8	0.0933	33.11		.422	9.20	0.2105	0.2695	[illegible]
9	0.1299	44.37	$\bar{1}.753$	.566	12.33	0.2345	0.3003	$\bar{1}.47$[illegible]
10	0.1640	56.01		.714	15.58	0.2437	0.3120	
11	0.2255	77.00	$\bar{1}.992$	.981	21.39	0.2546	0.3260	$\bar{1}.5$[illegible]
12	0.1429	48.50		.618	13.48	0.2380	0.3046	[illegible]
13	0.0994	33.98	$\bar{1}.636$	.433	9.44	0.2174	0.2783	$\bar{1}.$[illegible]
14	0.0580	19.70		.251	5.47	0.1676	0.2144	
15	0.0420	14.38		.183	4.00	0.1496	0.1915	
16	0.0273	9.35		.119	2.60	0.1326	0.1697	
17	0.0140	4.80		.061	1.33	0.1142	0.1461	
18	0.0051	1.77	$\bar{2}.362$	.023	0.49	0.0926	0.1185	$\bar{1}.$[illegible]
19	0.0037	1.26	$\bar{2}.204$	.016	0.35	0.0821	0.1051	$\bar{1}.$[illegible]

TABLE III.

CARBON TETRACHLORIDE VAPOUR.

Gel sample 3.8216 gms.

P_0 = 142.3 mm @ 30°C. σ = 24.6 $\frac{\text{dyne}}{\text{cm}}$ @ 30°C.

Exp.	Wt. Vapour	P mm	P/P_0	P/P_0	$\frac{x}{m}$	$\frac{v}{m}$
1	0.0244	3.0 $\bar{2}.324$	.0211	0.517	0.178	0.112 $\bar{1}.04$
2	0.0437	5.37	.0377	0.925	0.212	0.127
3	0.1119	13.7 $\bar{2}.987$	.0971	2.37	0.253	0.159
4	0.1857	22.8	.1600	3.93	0.298	0.188
5	0.2500	30.7 $\bar{1}.338$	.218	5.29	0.313	0.197
6	0.3484	42.8	.301	7.37	0.337	0.212
7	0.5154	79.7 $\bar{1}.748$	.560	13.73	0.397	0.244 $\bar{1}.387$
8	0.7254	89.1	.626	15.34	0.405	0.255
9	0.8212	100.1 $\bar{1}.8$	.709	17.37	0.413	0.260 $\bar{1}.4$
10	1.1481	141.0	.991	24.28	0.450	0.283
11	0.3881	60.0 $\bar{1}.625$	.422	10.33	0.372	0.234
12	0.1522	18.7	.131	3.22	0.280	0.176
13	0.0991	12.2	.086	2.11	0.243	0.153
14	0.0771	9.5 $\bar{2}.82$	.067	1.64	0.230	0.145
15	0.0333	4.1	.029	0.71	0.189	0.119
16	0.0134	1.7 $\bar{2}.07$	.012	0.30	0.152	0.096

TABLE IV.

BENZOL VAPOUR.

Gel sample 4.923 gm.

P_o = 120.2 mm @ 30° C. $\mathcal{T}$ = 29.0 $\frac{\text{dyne}}{\text{cm}}$ @ 30° C.

Exp.	Wt. Vapour	P mm	P/P_o	$P^{\mathcal{T}}/P_o$	$\frac{x}{m}$	$\frac{v}{m}$
1	0.487	117.8	.980	28.42	0.247	0.280

TABLE V.

Saturation Values of $\frac{v}{m}$.

H_2O	.3156
C_2H_5OH	.3266
CCl_4	.285
C_6H_6	.281

VI. Discussion of Results.

1. The accompanying graphs show the relationships.

Fig. IV.

$\frac{x}{m}$ values of H_2O adsorbed   partial pressure H_2O vap.

Fig. V.

$\frac{x}{m}$ values of C_2H_5OH adsorbed   partial pressure C_2H_5OH vap.

Fig. VI.

$\frac{x}{m}$ values of CCl_4 adsorbed   partial pressure CCl_4 vap.

Fig. VII.

$\frac{v}{m}$ values of all liquids   partial pressures

Fig. VIII.

$\log \frac{v}{m}$ log. pressure

Fig. IX.

$\log \frac{v}{m}$ log. corresponding pressures P/P_o

Fig. X.

$\log \frac{v}{m}$ log. corrected corresponding pressures P/Po

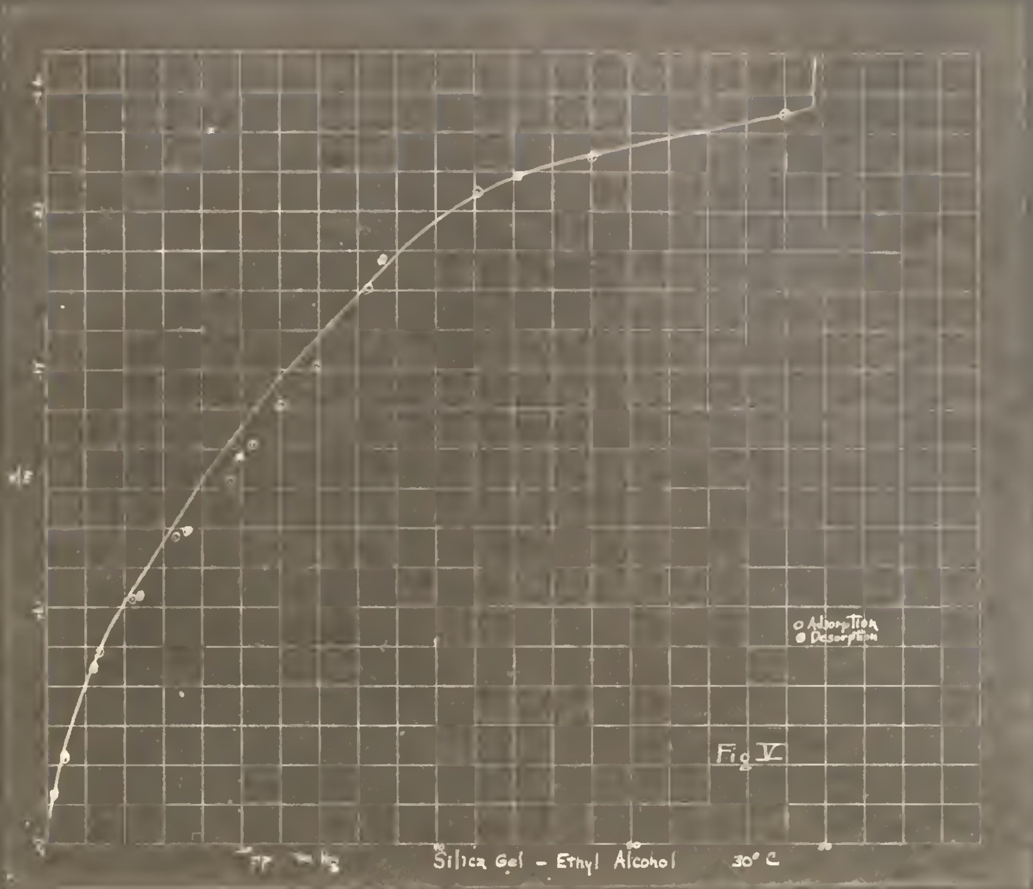


Fig V

Silica Gel - Ethyl Alcohol 30° C

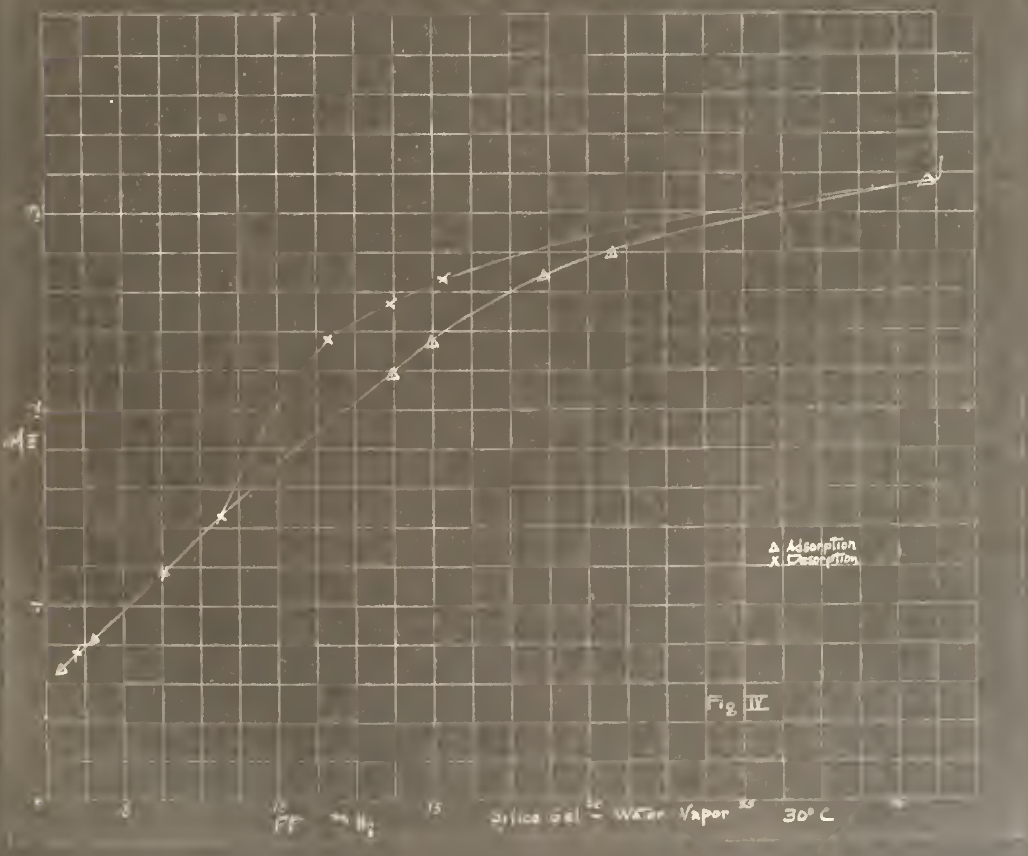


Fig IV

Silica Gel - Water Vapor 30° C

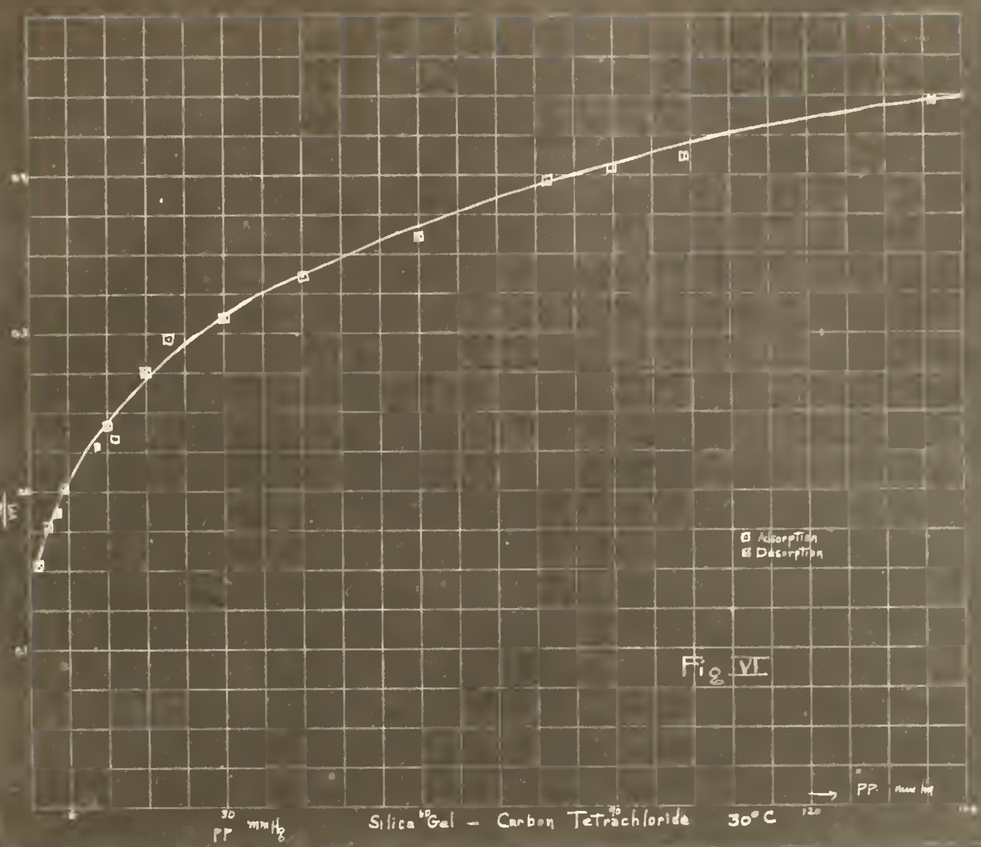


Fig VI

Silica Gel – Carbon Tetrachloride 30° C

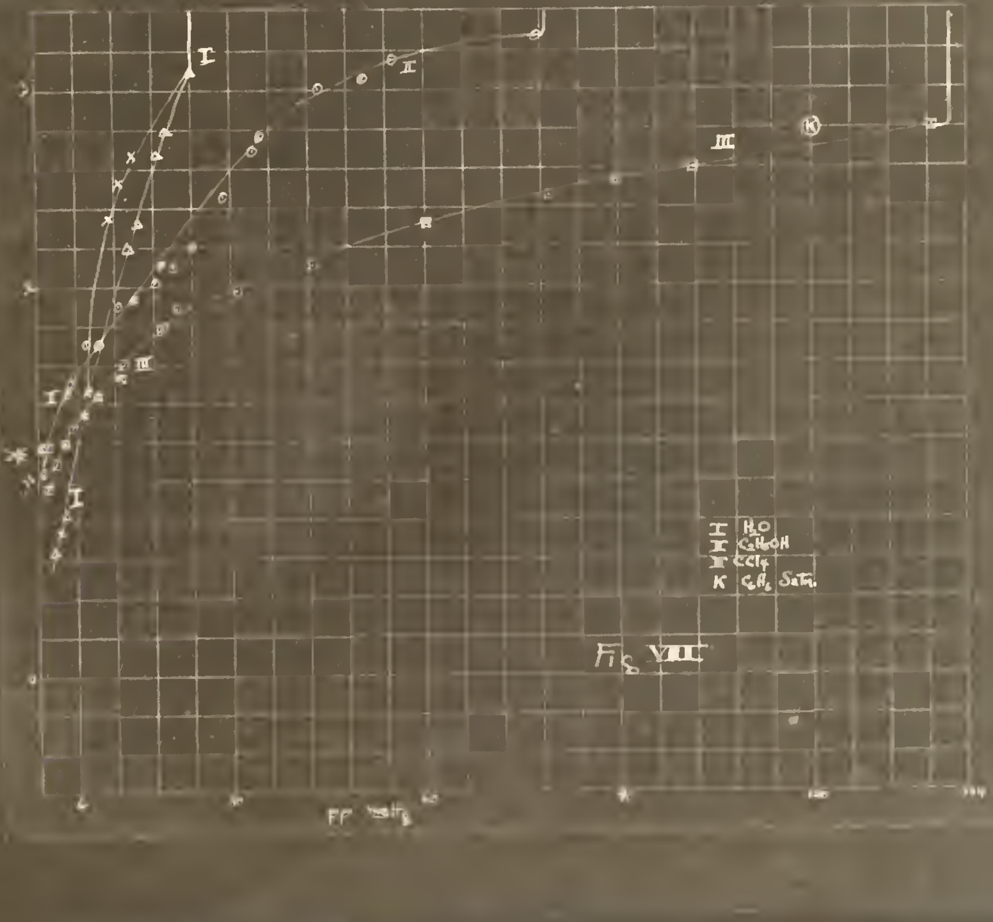


Fig VIII

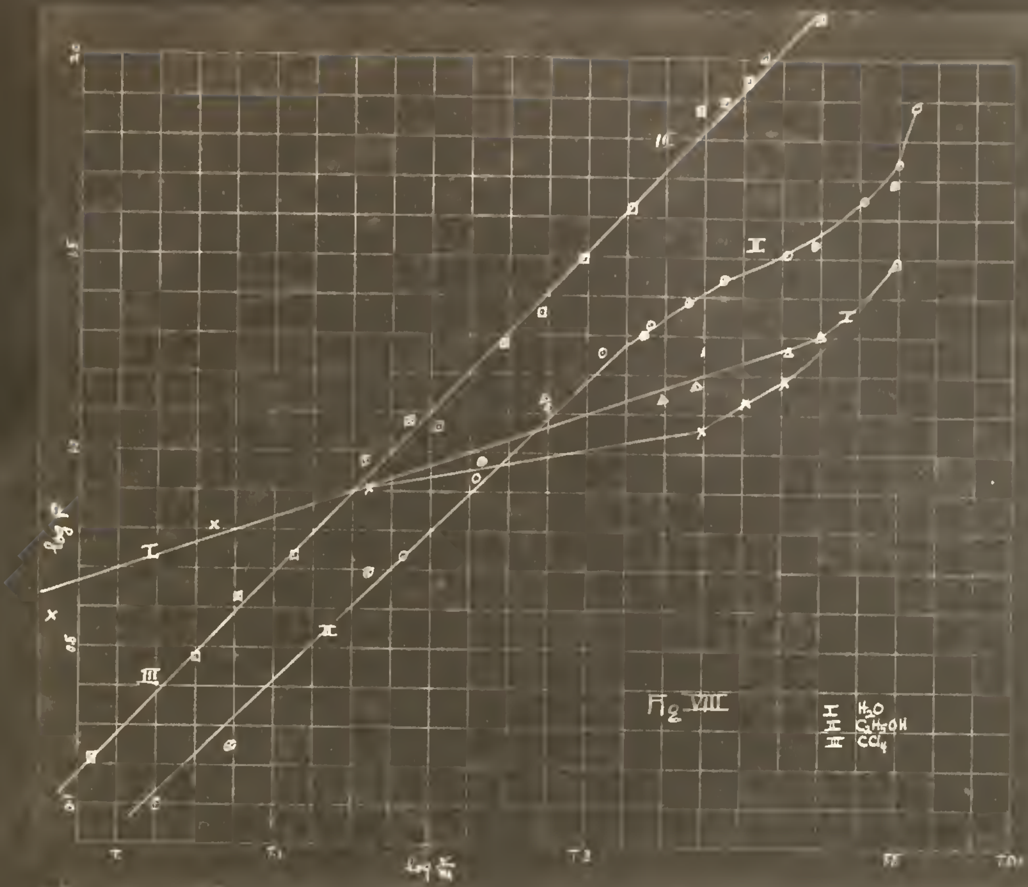


Fig. VIII

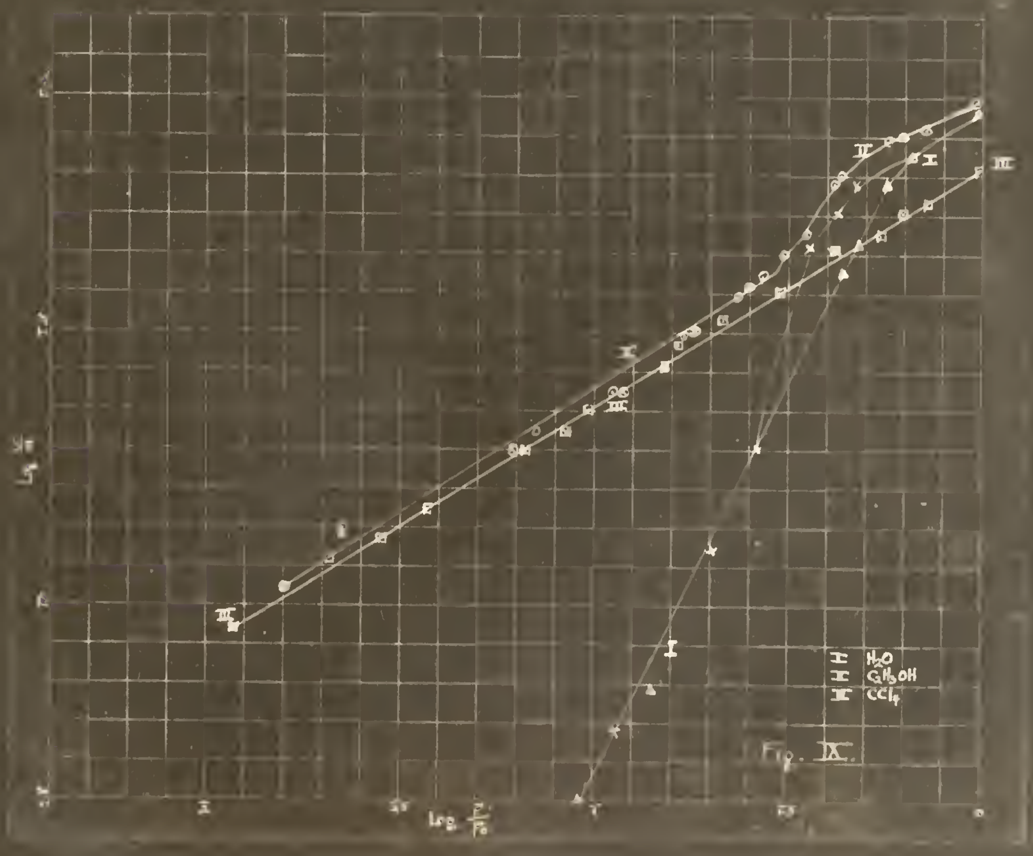
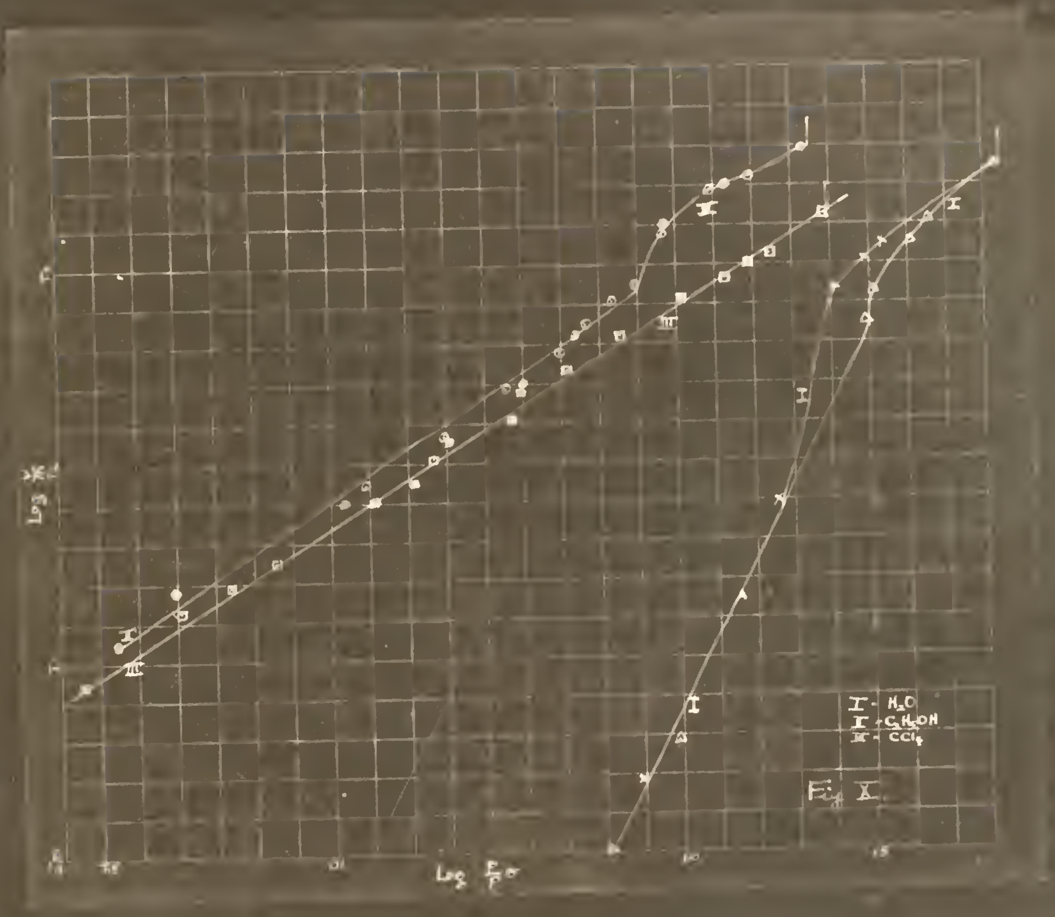


Fig. IX.

I - H_2O
II - C_2H_5OH
III - CCl_4
I
II
III
Fig. X
Log $\frac{P_0}{P}$
1.0
1.5

The above results are of interest in light of the explanation that has been advanced in this laboratory to account for the adsorption of gases by porous bodies. It was found in the case of the adsorption of both sulphur dioxide[1] and ammonia[2] by silica gel that the experimental results were in harmony with the idea of the influence of capillarity on the condensation pressure, i.e. the ratios of the partial pressure to the vapor pressure. The results of our earlier studies led us to the belief that the volume of liquid adsorbed was proportional to the condensation pressure as well as the surface tension of the liquid.

We at first attributed the influence of surface tension on the adsorption to the well known antibatic relation between surface tension and compressibility. Our reasoning was that under similar condensation pressures liquids of low compressibility would be more strongly adsorbed due to their smaller dilation. Whatever the exact explanation of the mechanism of adsorption, it can be easily shown that surface tension plays an important role in the

1. McGavack & Patrick. loc. cit.

2. Davidheiser & Patrick

condensation of a vapour to a liquid, and that, furthermore, condensation will occur in a capillary more readily the higher the surface tension of the condensed liquid. If we place capillary tubes into two liquids of the same vapour pressure and density but of different surface tension, the capillary rise will be greater in the case of the liquid having the larger surface tension. That is to say that the reduction of vapour pressure due to capillarity will be greater with the latter liquid. Therefore at equal values of condensation pressure condensation will take place preferably with the liquid exhibiting the largest surface tension. This accounts most satisfactorily for our observation that adsorption of vapors is greater with increasing value of the surface tension of the condensed liquid.

For the present discussion it is sufficient to begin with a consideration of the experimental results as given graphically in Fig. X. There it is to be noted that the values of adsorbed liquids in the case of ethyl alcohol and carbon tetrachloride are nearly equal at corresponding pressures. However water presents a most anomalous behaviour

and apparently is in utter disagreement with our theoretical views. It is noticed that the volume of water adsorbed per gram of gel is much less than that of the other two liquids at similar condensation pressures. This discrepancy is most marked at low partial pressures, but at the saturation pressure the volume of water adsorbed is practically identical with that of alcohol.

The failure of water to behave in a manner supporting our views, on further inquiry gives additional evidence of the validity of our explanation that the adsorption of a vapor by a porous body is due to the reduction of vapour pressure of the condensed liquid. This reduction of vapour pressure we have attributed to the tendency of the condensed liquid to present a minimum surface, which results in the liquid being dialated or at least subject to a reduction of internal pressure. Most liquids exhibit an increase of viscosity with increased pressure. Water, however, is an outstanding exception and therefore must show an increase of viscosity with decreasing pressure. If this be true, it is evident that in the case of the first amounts of water adsorbed the capillary influence is at a maximum, i.e., the

water is under a high reduction of internal pressure, and therefore must be very viscous. This increase of viscosity prevents true equilibrium from being reached and thus explains the low values of the amount of water adsorbed. On the other hand the effect becomes less marked with higher pressure until at the saturation pressure we find water behaving in a normal manner. It is obvious that near the saturation pressure the viscosity of all the liquids must be normal inasmuch as the capillary influence is then negligible.

This view is greatly strengthened by a study of the time necessary to reach apparent equilibrium in case of the different liquids. In the case of benzene, carbontetrachloride and alcohol equilibrium was reached very quickly, always within a few hours. An entirely different result was obtained with water, it being sometimes necessary to continue the flow of water vapour as long as three days. Furthermore, water was the only liquid showing a marked difference (hysteresis) in the amount of water adsorbed between the hydration and dehydration curves.

SUMMARY.

1. The adsorption of vapours of alcohol, benzene, carbon tetrachloride, and water by silica gel were investigated by a dynamic method.

2. It was found that with the exception of water the adsorption of these liquids was in accordance with the influence of capillarity on the condensation of vapour.

3. No hysterisis was observed except in the case of water. This observation being in strong opposition to the work of Anderson and Zsigmondy.

4. The slowness of the adsorption and deadsorption of water vapour was attributed to the increase of viscosity of the adsorbed water due to the decrease in internal pressure.

5. An explanation was offered for the lack of absolute agreement in the volumes of the four liquids adsorbed at the satruation pressure.

BIOGRAPHY.

Lawrence Hall Opdycke was born in 1891 in West New York, N. J. He attended the public schools in that town and High School in the town of Union, N. J. He received the degree of B. S. in Chemistry from Rutgers College in 1913 and A. M. degree in 1916 from Columbia University. He was engaged in Industrial Chemical fields at various times and was Instructor in Chemistry at the Pennsylvania State College 1916-17. In the interval 1917-19 he was Chief Inspector of Explosives in the Pacific Coast Section, U. S. Army Ordnance. He has been matriculated at the Johns Hopkins University since September 1919.